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THE ABSORPTION AND FLUORESCENT SPECTRA
OF
SODIUM VAPOUR.

DISSERTATION
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BY

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The Absorption and Fluorescent Spectra
of
Sodium Vapour.

I. Introduction.

According to the investigations of Eder and Valenta, Kayser and Runge, Evershed, Liveing and Dewar, Roscoe and Schuster, Wiedemann and Schmidt, and the recent work of Percival Lewis there appear to be about seven different spectra of sodium; - the spark, the arc, spectrum in discharge tubes, kathodo-luminescent, thermometric, fluorescent, and absorption spectrum. It is quite probable, however, that a careful comparison of these apparently different spectra of sodium will result in reducing the number, but as yet such a study of the relation between them has not been made.

The present paper has for its purpose: First, the study of the absorption spectrum of sodium vapour under different conditions of density and length of absorbing column, and the measurement of the wave lengths of the principal absorption lines. Second, the study of the fluorescent spectrum of this vapour; the light which produces this fluorescence, and the measurement of the wave lengths of the principal lines. Third, a comparison of the absorption and fluorescent spectra in order to determine the relation between them, if there be any.

II. Absorption Spectrum.

(a) Historical.

It appears that the absorption spectrum of sodium vapour was first studied by Roscoe and Schuster[*] in 1874. In their work, the sodium was heated in an atmosphere of hydrogen, and confined in iron tubes. As a source of light a lime light was used, and the spectrum observed with a Steinheil spectroscope the resolving power of which was just sufficient to separate the D lines. They speak of the absorption spectrum as consisting of three groups of bands α, β, γ. which appear as the density of the vapour is increased, in the order α, γ, β. They have also given a few measurements of the more refrangible edges of these bands, which can only be regarded as roughly indicating their relative position; but a detailed study of the structure of these bands was not attempted. This spectrum seems also to have been noted by Lockyer[**] in his work on the absorption of metallic vapours but he has not given any description of the phenomena, or measurements of wave lengths. In 1878 the absorption spectrum of sodium vapour was again studied by Liveing and Dewar[***] in connection with their investigation "On the reversal of the lines of metallic vapours".

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[*] Proc. Roy. Soc. XXII, p. 362, 1874.

[**] Lockyer, Proc. Roy. Soc. XXII.

[***] Liveing and Dewar, Proc. Roy. Soc. XXVII, 1878.

Their method consisted in observing the effect of the absorption produced by the vapour on the continuous spectrum emitted by the sides and end of the tube in which the volatilization took place. The tube which was of iron coated with borax, was inserted in a vertical position in a furnace. Hydrogen was introduced in the upper part of the tube so that it floated upon the vapour without producing convection currents in it, a frequent source of trouble in the case of the volatilization of sodium in an atmosphere of hydrogen in horizontal tubes. They have described the general phenomena of the absorption of the vapour studied in this manner without, however, any careful measurements of the absorption lines. In a later investigation• Liveing and Dewar attempted a quantitative study of the absorption of sodium vapour, with regard to thickness of layer, density and temperature of the vapour. They employed iron bottles in a similar manner as the tubes were used above. It was found, however, that determinations of the density of the vapour made in iron tubes are worthless as it appears that iron takes up the vapour of sodium. Tubes of platinum were then used but even then they were unable to determine their

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• Liveing and Dewar, Proc. Roy. Soc. XXIX, 1879.

temperature or confine the vapour to a definite length of column as sodium vapour at this temperature attacks all known transparent substances.

Recently the absorption spectrum of sodium has been studied by Professor R. W. Wood* in connection with his work on the anomalous dispersion of sodium vapour. Photographs were taken with a Rowland concave grating of 10 feet focal length, but no measurements of wave length were made, since he hoped to obtain better photographs. In a later paper** he has called attention to the fact that with a very dense vapour a heavy absorption line appears at about 552. Unfortunately in the present work the author was unable to keep the vapour dense enough for a sufficient interval to photograph this line, or to obtain it visually with the concave grating of so long a focal length, but its position was verified with a concave grating of 7 feet focal length. It was at the suggestion of Professor Wood that the author took up this investigation, and all the work both on the absorption and fluorescent spectra was done with his assistance and under his personal supervision.

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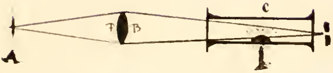
* Proc. Roy. Soc. 69, p. 157, 1901-1902.

** Phil. Mag. March 1902, p. 359.

Apparatus and Method.

Visible Spectrum: In the present investigation the general arrangement of the apparatus for a study of the absorption spectrum is as shown in the figure, where A is the source of light, B a double convex lens (quartz or glass) of long focus, so placed that the source A and the slit F of the spectrograph were conjugate foci, the distance A P being about 54 cm. and the distance P F about 90 cm. C is the tube in which the sodium was vaporized.



The spectrograph used was a Rowland concave grating of 13 feet 3 inches focal length, having a ruled surface of 6 inches with 15000 lines to the inch. The grating was furnished with the usual Rowland mounting and provided with a camera and shutter of the usual form. The plates used were "Seed's gilt edge No. 27", Seed's Orthochromatic", and "Cramer's Isochromatic", specially mounted on lantern slide glass and cut in the proper size 11 1/2 x 1 1/4 inches. An attempt was also made to use Cadett Spectrum plates, Seed plates No. 27, stained with Benzo Nitrol Brown according to the method of Ives; and also Seed plates sensitized by the stain furnished by the Seed Co. for photographing the absorption lines in

the red but all efforts of this nature failed.

As a source of light it is desirable to use one giving a spectrum which is as nearly continuous as possible. The hot pole of a vertical carbon arc was first used, likewise of a right angled carbon arc. Much trouble is experienced in the use of either of these forms of the carbon arc due to the difficulty of keeping only the image of the glowing pole on the slit without at the same time getting some of the flame, and even under the best conditions the spectrum of the hot pole contains a few strong lines which are sufficient to complicate the results obtained in absorption photographs unless great care is taken. A form of light known as "sun light", which consists of two carbon poles mounted in a block of marble in such a way that the arc is formed across the face of the marble,was next tried. This gives an extremely intense source and a fairly continuous spectrum but here we are troubled with the calcium channels in the green which occur in the same region as the green absorption channels of sodium, so that this form of a source had to be abandoned. A Nernst filament run by a 110 volt alternating current was found to be very satisfactory for this work as it gives a perfectly continuous spectrum. The only disadvantages in its use were that it required a longer exposure for the photographs and givesno ultra-violet radiation be-

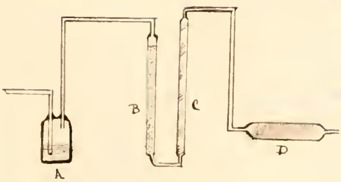
yond 2700 neither of which are serious faults. It was therefore used as the source of light for all work in the visible spectrum or at least a complete set of plates was made with it and all plates taken with the carbon arc referred to these in order to separate the arc from the absorption lines. As a comparison spectrum that of the iron arc was used.

The sodium used in the experiments was ordinary metallic sodium, which was found to be fairly free from impurities. Nearly all commercial sodium contains slight traces of potassium but with a few exceptions the samples here tested were found to be very nearly free of traces of this metal. In one or two samples, however, a reversal of the strong potassium lines 4047.36 and 4044.29 appear in the photographs. Samples used later in the experiments, however, failed to show reversals of any of the potassium lines. Care was always taken to remove all the oxidized surface of the metal, and the hydrocarbon solution in which the metal was kept. About .5 to 1 gram of the metal was used in each experiment.

The tubes in which the sodium was vaporized were of sheet iron and steel, although some experiments were made using glass tubes. The glass tubes, however, soon go to pieces under the action of the heated vapour so that it was found better to use the iron tube whenever possible. The tubes

which were found to be the most satisfactory were those made of Shelby seamless tubing, in diameter 3/4 inches and 1 3/8 inches and guage 16 and 20. The tubes were from 18 inches to two feet in length. The ends of the tubes were closed with plate glass or a good quality of thin glass sealed on with sealing wax. Small side tubes were brazed in the large tubes for introducing hydrogen or for exhausting.

In the first series of experiments the sodium was vaporized in an atmosphere of hydrogen, in order to prevent any oxidation of the metal. The slightest trace of oxygen in the tube is sufficient to produce a dense smoke of sodium oxide which attacks the glass ends of the tube and makes them opaque. The hydrogen was prepared by electrolysis using a cell with cylindrical lead electrodes in a 25% solution of H_2SO_4. Such a cell was found to give both a good current of the gas and sufficiently pure for most purposes. This gas was dried by passing in order through a H_2SO_4 bottle A, calcium chloride tube B, and a tube C containing P_2O_5 and glass wool. In order to remove all traces of oxygen the hydrogen was also passed through the tube D containing copper gauze which was heated until it was a bright red. A Kipp generator was also



used in some of the later experiments in which hydrogen was used and the gas from it when passed through the above system of drying tubes was found to be very good for the purpose desired. In the later series of experiments in which the sodium was vapo rized in a vacuum, the tubes were exhausted with a Toepler pump to a pressure of from 1 to 5 mm. which was found sufficient to eliminate the formation of sodium oxide in the tubes.

Two methods of heating the tubes were employed. One in which a Bunsen burner was played upon the tube directly under the lump of sodium. The other in which the tube was wound with a coil of No. 20 iron wire, insulated from the tube by asbestos, and the whole packed in asbestos in a tight iron box. The later method is preferable for some reasons; namely, the temperature of the vapour can be kept nearly constant for quite a long interval of time, and the density of the vapour is more nearly uniform throughout the cross section of the tube. A Bunsen burner is better for some experiments, however, where a dense vapour of short column is desired. With it the sodium does not distil so rapidly to all parts of the tube and with careful regulation of the flow of gas in the burner it was used very successfully in many of the experiments.

The method of experimenting consisted simply in preparing a tube as described above, vaporizing the sodium, until the

vapour density and length of the column of vapour was sufficient to give the particular part of the spectrum studied and then to keep this condition of the vapour perfectly constant throughout an exposure. In order to do this the spectrum of the higher order than the one photographed was observed throughout the exposure by means of an eyepiece and the source of heat varied so as to maintain the conditions perfectly constant. The length of exposure ranged from twenty to sixty minutes according to the part of spectrum, the plates, and the degree of absorption used. To keep the conditions constant through such an interval of time is difficult indeed and required the repetition of the experiments many times in order to obtain sharp photographs, in which the conditions remained the same throughout an exposure.

It was found that the best results were obtained with the absorption spectrum when the width of the slit was 0.065 mm. The width of the slit for the iron comparison spectrum was 0.030 mm. In order, however, to eliminate any errors due to changing the width of slit photographs were taken using a slit of 0.030 mm. for both the absorption and iron spectrum, and the measurements of the two sets of plates were compared. The plates were measured on the dividing engine, provided with a diamond shaped reticle, the method of using which has been described by Humphreys and Mohler[•].

[•] Humphreys and Mohler. Astrophysical Journal. Oct. 1897 p.169.

The plates were taken only in the first spectrum and an accuracy of .05 of an Ångström unit is all that is claimed for the wave-lengths.

Ultra-violet spectrum. The ultra violet absorption spectrum was investigated in a similar manner using, however, glass and iron tubes closed at the ends with quartz plates. A few photographs were taken with the grating used above, with the carbon arc as a source, and with the vapour just dense enough to reverse the D lines. The length of the exposure thus required was found to be too great, so that for a further study of the ultra violet absorption a quartz spectrograph was employed using as a source of light either a cadmium spark or a carbon arc.

The Spectrum. General Description.

When a lump of sodium is placed in the tube and heated as described above, the first appearance of absorption lines is at the D lines 5896.16 and 5890.19 which appear as two extremely fine lines. As the amount of vapour in the tube increases these lines broaden. D_2, however, is stronger and broader and broadens more rapidly than D_1. When the D lines are strongly reversed 3303.07 and 3302.47 reverse, also 2852.91 and 2680.46. A further increase of the vapour until the point

where the D lines can just be separated, causes 3303.07 and 3302.47 to form a single broad line, and brings out strong 2852.91 and 2680.46, also causing a reversal of the double lines 2593; and 2543 and 2511. These lines are those of the principal series of sodium and are reversed in order 5890, 5896, 3303, 2852, 2680, 2593, 2543, 2511, as the density of the vapour is increased the intensity of the lines of the series decreasing also in the same order.

While the D lines are about 2 or 3 Ångström units in width a series of absorption bands appear in the blue green. These begin as nine bands, the heads of which point toward the violet end of the spectrum, i. e. in each band the absorption decreases from the head toward the longer wave lengths. The heads of the bands as they first appear are:

I. 4783.35
II. 4809.92
III. 4837.72
IV. 4865.60
V. 4894.94
VI. 4932.97
VII. 4962.96
VIII. 5001.94
IX. 5040.71

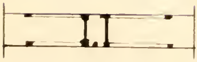
There is also evidence of absorption lines in the first seven bands which do not come out strong, however, but appear as slight shading in the bright back ground. In band I can be seen the strong line 4793.10, in band II 4820.72, in band IX 5053.50 and in band VII 4979.28, which appear as fainter heads of small bands into which the others break up. Bands V and VI are about the center of the absorption region. (See Fig. I Plate). A very slight increase in the amount of vapour in the tube is sufficient to bring out the heads of these bands very strong together with the fainter heads in the bands themselves. The bands are now seen to be composed of a series of strong lines together with a series of fine lines and in some of the bands there is the appearance of a superposition of the two series. At this time the region of absorption extends from about 4600 to 5200, a series of 3 bands the more refrangible edge of which are broken up into smaller bands appearing from 5079-5200, and a series of ten or twelve bands each of which is divided into smaller bands and containing strong lines appearing from 4780-4600. This whole group of lines and bands from 4600-5200 will be called for convenience group A. This group of lines appear when the color of the transmitted light is a yellow green, and also at the time when the fluorescence of the vapour first appears.

These lines have therefore been carefully studied in order to furnish a basis for the work on fluorescence of the vapour.

At this stage a series of channeled bands extending from about 6004-6800 make their appearance, the absorption in the neighborhood of the D lines is now a hazy band about 40 or 50 Ångström units in width, with a series of lines on each side of it from 5700-5860 and from 5930-6004. These series of lines are not channeled but appear as strong absorption lines. With a further increase in density of the vapour the region between 4600 and 5300, and all the region of longer wavelengths than 5700 are totally absorbed, and a series of lines come out between 5300 and 5700; and in the region from 4600 to 4300 a series of small bands appear with indications of lines up as far as 3700. The effect of still further increasing the density of the vapour was never successful as it required a length of exposure so long that the conditions could not be maintained constant during this time, in fact, it was found difficult to maintain the condition of the vapour constant for a time sufficient to photograph the series 5300-5700.

Variation with density and length of absorbing column.

We have used the expression above, "as the density of the vapour was increased". Strictly speaking, however, the length of the absorbing column of the vapour was increased slightly at the same time, for in order to increase the density of the vapour the tube was raised to a higher temperature immediately surrounding the lump of sodium. As the temperature of the vapour was increased it would condense at points further along the tube, due to both the increase in the temperature of the vapour and at the same time the rise in the temperature of the parts of the tube removed some distance from the middle of the tube due to the conduction of the tube. In order, therefore, to separate the phenomena due to variation in density, and variation in the length of the absorbing column, the author has devised several methods, all of which failed since it is necessary to confine the vapour with some transparent substance, and sodium vapour at the temperature here used attacks all transparent substances. A tube of the form shown in the figure, consisting of a steel tube 1 3/8 inches in diameter and 2 1/2 feet long, inside of which slipped two smaller steel tubes A and B carrying caps in which glass plates were placed, was first used. The large tube was closed with



glass plates at the end and exhausted to 1 mm. after being washed thoroughly with dry hydrogen. The tube was wound with iron wire and heated to a red heat. The sodium vapour condenses on the glass plates until they become hot and then the vapour attacks the glass. Glass bulbs of different kinds of glass were next used. These bulbs were dried and a small piece of sodium placed in them. The sodium was carefully prepared by volatilizing it in a vacuum, and condensing all hydro carbon vapours in another part of the tube. The bulbs were exhausted to 1 mm. and heated with iron coils in a constant temperature air bath. By using bulbs in this way it would be possible not only to keep a constant and known length of the column of vapour at a uniform density, but also to determine the density of the vapour according to a method used by Jewett.* Unfortunately at the temperature at which the vapour is dense enough to bring out the channel spectrum, the sodium vapour violently attacks the glass making it opaque, so that all quantitative measurements of density and length of vapour column had to be abandoned. In order to see if an increase in the length of the absorbing column of the vapour would produce the same effect as an increase in the density of the vapour a steel tube five feet in length was used. In this were placed eight lumps of sodium of exactly

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* Jewett - Phil. Mag. Nov. p. 546, 1902.

the same size (about 3 grams each) at intervals of about 30 cms. Under each lump was placed a Bunsen Burner, the burners being regulated to give the same flame, and just sufficient so that when one was placed under the first piece of sodium the vapour was dense enough to reverse the D lines as two strong lines. The other burners were then placed under the tube in succession, and the same phenomena as to broadening of the D lines and appearance of channel spectrum took place just the same as when the density of the vapour was increased. It would be interesting to know if the effect of increasing the length of the absorbing column is the same as increasing the density in the sense of whether doubling one is the same as doubling the other. This, of course, cannot be determined since here again we are required to find the column of vapour by means of a transparent spectrum which cannot be done.

III. Fluorescent Spectrum.

Historical:-

That sodium vapour when illuminated by white light becomes luminous or fluoresces was first observed by Wiedemann and Schmidt[*] and later studied and described by them[**].

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[*] Wiedemann and Schmidt. Beibl. 20, p. 693, 1896.

[**] Wied. Ann. 57, 447, 1896.

Astrophys. Journ. 3, 207, 1896.

The method employed was to volatilize the metal in glass bulbs previously exhausted, illuminate the vapour with sun light and observe the fluorescence with a spectroscope, at an angle with the direction in which the sunlight was focused upon the vapour. They repeated their observations later[*] using a spectroscope of greater dispersion. In this work they conclude that the fluorescent spectrum of sodium vapour consists of three parts; (1) a bright line in the yellow coinciding with the D lines; (2) a band (not channeled) in the red from 675 to 602.5 ; (3) a series of bands in the green between 527.6 - 480.5 . twelve of which they have measured. Owing, however, to the comparatively low dispersion which they were able to use, these measurements can only be regarded as indicating roughly the position of the bands to within about 10 Ångström units. The fluorescence of the vapour obtained in glass bulbs is quite faint and much difficulty is experienced in using this method. In as much as the fluorescence of vapours is of much theoretical interest, and as Wiedemann and Schmidt have pointed out may also play some part in the explanation of the spectra of the corona, certain forms of prominences, etc., it seemed desirable to obtain more definite results on the fluorescence of

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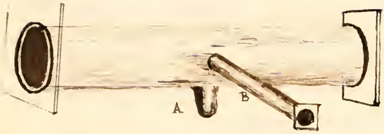
[*] Verh. der phys. Gesellsch. zu Berlin, 16, p. 37-40, 1897.

sodium vapour, both as to the color of the light producing this fluorescence and the wave lengths of the bands and lines in the spectrum.

The fluorescence of sodium vapour has also been observed by Professor Wood.[*] His observations are similar to those of Wiedemann and Schmidt. He obtained in his experiments the bright yellow band at the D lines, the red and green fluorescent bands with the channels in the green, but no measurements of wave length were made.

Apparatus: In order to do this a tube was designed according to the suggestions of Professor Wood which was found to be all that could be desired as the fluorescence obtained in this way was very intense compared with that obtained in glass bulbs or other forms of tubes. The tube used was of the form shown in the figure. The large tube was 3 inch 16 guage, Shelby seamless tubing 2 feet in length. At B a tube 3/4 inch in diameter and about 10 inches in length was brazed in the large tube at right angles to its length. A is an iron crucible 3/4 inches in diameter and



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[*] Proc. Roy. Soc. 69, p. 157, 1901-1902.

3 inches in length, made by boring out an iron cylinder. This crucible was brazed in the large tube at right angles to it and also to the tube B, and extending up into the large tube just so that its edge can be seen through B. The tube A was then filled with sodium, the ends of the large tube closed with plate glass, and the tube B with lantern slide glass, and then exhausted to a pressure of about 5 mm. Before removing from the pump the sodium was melted in order to pump off the hydrocarbon vapours. The tube was then placed with A vertical and B horizontal and sunlight focused over the tube A at a point directly opposite B. A Bunsen burner or blast lamp was placed under A. When the vapour above A becomes dense enough for the channeled spectrum in the blue green to appear in the absorption spectrum as observed directly through the large tube, a beautiful green band of light in the focus of the sunlight is seen on looking in the tube B. As the density of the vapour is increased the intensity of this fluorescence is increased the color of the light being a deep green. The intensity of the fluorescent light obtained in this way was from fifteen to twenty-times that of the fluorescence obtained in bulbs or other forms of tubes. The reasons of this are: first, with glass bulbs it is impossible to obtain the density of the vapour which can be used in this method, and secondly, with other

forms of tubes and with glass bulbs the light producing the fluorescence must pass through a column of vapour which absorbs to some extent the wave lengths producing the fluorescence while with the form of tube used the vapour through which the light passes is only that directly over the tube A and in which the fluorescence is observed.

In order to study the fluorescent spectrum a Steinheil spectroscope of two prisms the resolving power of which was sufficient to separate the D lines, was first used. Photographs of the spectrum were obtained with this instrument, but all of them were unsatisfactory. A Rowland concave grating of two inches ruled surface, 15000 lines to the inch and one meter focus was then used. This grating was mounted in a box in a fixed position, at a distance of 1 meter from the slit, and the plate holder placed in a fixed position and cut to the proper curve to give the first spectrum in focus on the plate. The spectrum obtained in this way is not strictly normal but was found to be very approximately so. To eliminate any error, due to the spectrum not being normal, the plate was calibrated throughout its length. The plates used were Seeds Orthochromatic films. These were measured in the same manner as described above using, however, as ref-

erence lines those of the solar spectrum which always appeared in the blue and violet on photographs of the fluorescence, due to reflection from small particles of sodium oxide which appeared at times in the tube. The lengths of exposure for the fluorescent spectrum were from one to two hours, according to the density of the vapour, and the intensity of the sunlight. No photographs were obtained of the fluorescent band in the red, but several photographs of the channels in the green and blue green were obtained, (see Plate).

The Spectrum.

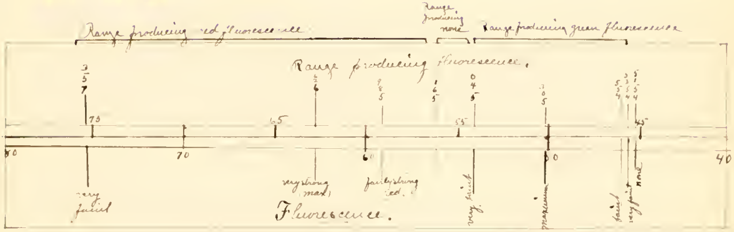
The fluorescent spectrum of sodium vapour when observed with a Steinheil spectroscope corresponds in general with the description of Wiedemann and Schmidt. First a band in the red from about 670-600 . When the fluorescence is very intense a series of channels could be seen in this band but they were too faint to be measured and were only seen in a very few experiments when the conditions for very intense fluorescence were best. This band is described by Wiedemann and Schmidt as not channeled . It appears that these channels only come out when the vapour is very dense. Second, on each side of the D lines there is a narrow faint band just sufficient to show the D lines as a strong dark line. Wiedemann and Schmidt obtained on the other hand a bright line in the yellow coinciding with the D lines.

This line was never observed by the author, as the D lines always came out as a dark line on a faint back ground. Third, a series of channeled bands extending from 5340 to 4600. This series is divided into three groups: (1) Those from 5340 - 5080 consisting of five or six broad hazy bands, which shade off equally on the two sides; (2) Those from 5080-4865 a group of channeled bands the heads of which point toward the red, i. e. they are strongest on the less refrangible side and shade off toward the shorter wave lengths. These bands are divided into secondary bands and contain also a few strong lines; (3) those from 4865-4600 which appear as strong lines, but under greater dispersion they would probably be found to be small bands. There is also a series of four or five lines or small bands which appear in the photographs from 4600-4474, but on comparing with the solar spectrum they were found to be probably nothing but solar lines. Both series of channeled bands, 5080-4865 and 4865-4600 will be shown later to correspond exactly to the bands of Group A in the absorption spectrum.

The Light producing the Fluorescence.

In order to determine the relation existing between the incident light and that of the fluorescence and to find out what region of the spectrum of white light produces this intense fluorescence of sodium vapour, the vapour was illumin-

ated with monochromatic light, by means of the usual form of a two prism monochromatic illuminator, and the fluorescence observed as before through the side tube B described above. The light from such an illuminator is not strictly monochromatic but gives a band 10 Ångström units in width. This was sufficiently homogeneous, however, for the purpose here desired.



As shown in the figure, when the incident light is of shorter wave length than 452 μ no fluorescence is visible in the tube. At 453 μ a faint blue fluorescence is seen and as the wave length of the illuminating light is increased, the color of the fluorescence changes from blue to bluish green at the same time becoming more intense; when 503 μ is reached the fluorescence is then a deep green and very intense, a further increase in the wave length of the light causes the fluoreseence to decrease in intensity until 540 μ is reached. The wave length of the light producing the maximum green

fluorescence is then 503 μ which can be closely fixed as a change in wave length of 10 or 20 Angstrom units on either side of 503 produces a marked decrease in the intensity of the fluorescence. For the region 540 μ - 561 μ of the incident light little or no fluorescence can be seen in the tube; a very faint light can be seen, however, but probably due to particles of sodium oxide which at times are floating in the tube. The region 561 μ to 753 μ produces red fluorescence in the vapour, the wave length of the incident light producing the maximum red fluorescence being at 626 μ Light of wave length 5890 produces a fairly strong red fluorescence.

A small plane diffraction grating was then used for observing the fluorescence when the vapour is illuminated by monochromatic light as described above. A spot of the illuminating light was thrown on the end of the tube B so that it was visible at the same time with the fluorescent light. When the wave length of the illuminating light was about 455 μ the appearance as seen with the grating is as shown in figure (1) in which S is the deviated image of the blue spot of illuminating light, a the faint blue band of fluorescence of the same region as the light producing the

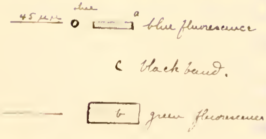


Fig. I.

fluorescence, and b a faint broad band of green fluorescence also produced by the blue illuminating light. Increasing the wave length of the illuminating light, until the deviated image S is a greenish blue (Fig. 2). S is moved downward toward the red; the very faint greenish blue fluorescent band a of the same wave length as S is seen; the green band b is now more intense its maximum having also shifted toward the blue.

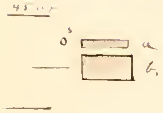


Fig 2.

With further increase in the wave length of the illuminating light, the band a disappears and we have b a green fluorescent band the maximum of which has moved further toward the blue (Fig. 3), and with still further increase in wave length of incident light, the maximum of b a green band coincides with S. (Fig. 4).

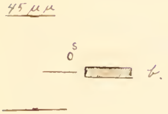


Fig (3)

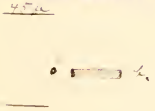


Fig (4)

When the wave length of the incident light is increased to about 530-540 μ a very faint green fluorescent band b can be seen the maximum of which lies farther toward the blue than S. (Fig. 5)

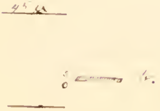
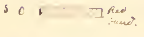


Fig (5)

This is very difficult to observe but the experiment was repeated several times with care and with the same result. This experiment indicates that when sodium vapour is illuminated with light of wave length about 530-540 μ , it gives off fluorescent light of a shorter wave length than that of the illuminating light, which, of course, is a contradiction to Stokes' law. It is probable then that in this particular region of the spectrum sodium vapour is an exception to Stokes' law.

For wave lengths of illuminating light between 540 and 560 μ produces no fluorescence and nothing but the image of S is visible. Between 560 and 753 red fluorescence appears. The spot S and the maximum of the red fluorescence band approach each other as the wave length of the incident light increases (similar to the observations above for the green) until the image S and the maximum of the red fluorescent band coincide. A further increase in the wave length of the light appeared to give the maximum of the fluorescent band further to the blue than to S. This observation is so difficult to make as the fluorescent is so faint that little importance is to be attached to it.



IV. The Relation between Fluorescence and Absorption.

The similarity between the fluorescent and absorption spectra of sodium vapour will have been noticed already and in particular in the region between 5300 and 4600 in which channeled bands resembling each other quite closely appear in both spectra. A comparison of the photographs of the two spectra shown and also fo the wave lengths of the heads of the bands and the principal lines, will show that this correspondence between the two is exact. It will be seen that the fluorescent spectrum is the negative of the absorption spectrum, i. e. bright lines and bands in the fluorescence corresponding exactly with dark lines and bands in the absorption. It is of much interest to know whether as indicated above the agreement in wave length is exact, in other words, to see whether the fluorescent spectrum is shifted relative to the absorption spectrum, and if no shift occurs to say within what limits. Photographs were therefore obtained with the two spectra on the same plate (see plate V). A careful comparison of the two spectra by this method shows the perfect correspondence of the bright lines of the fluorescent spectrum with the dark lines of the absorption spectrum. It also shows that if there is a "shift" in the fluorescent spectrum it cannot exceed 1 Ångström unit, for a

displacement of this magnitude would have been detected. It appears therefore that in this region from 5300-4600 sodium vapour absorbs light of certain definite wave lengths and radiates in what is called fluorescence exactly these same wave lengths, but as shown in the above experiments on the light producing the fluorescence, the green fluorescent bands can also be produced by the absorption of light of a different wave length , i. e. the absorption of light of wave length 4600 gives not only a fluorescent band 4600 but also a green fluorescent band. It is desirable to know whether this green fluorescent band is broken up into channeled bands which agree in position with the green channels corresponding to the green absorption bands shown in the photograph of the two spectra. This would require, however, photographs of the fluorescent spectrum when the vapour is illuminated with monochromatic light, which was not attempted since with monochromatic illumination the fluorescence is very faint.

From a comparison of the fluorescent and absorption spectra we have shown that there is no shift (within certain limits) of one relative to the other, which would indicate that there is little or no damping of the vibration absorbed

by the vapour and radiated in fluorescence. We can not conclude, however, that the damping is inappreciable for all wave lengths between 5300 and 4600 as we have shown that when the vapour absorbs light of a definite wave length, it may radiate in fluorescence not only this wave length but light of a longer wave length.

V. Conclusions.

The results of the above experiments may be summarized as follows:

(1) The wave lengths of the principal lines in the absorption spectrum of sodium vapour, which appear as the density of the vapour is increased, have been measured.

(2) It has been shown that the same effect in general is produced upon the absorption spectrum when the length of the absorbing column is increased as when the density of the vapour is increased, but no quantitative results could be obtained.

(3) The wave length of the principal lines in the green-blue fluorescent spectrum of sodium vapour have been measured.

(4) It has been shown that the bright lines of the fluorescent spectrum between 5300 and 4600 correspond exactly to the dark lines of the absorption spectrum in the same region.

(5) It has been shown that there cannot be a shift exceeding 1 Ångström unit in magnitude of the fluorescent spectrum between 5300-4600 over the absorption spectrum in the same region, thus indicating that when light of wave length (5300-4600) is absorbed by the vapour and radiated as fluorescent light, the damping of the vibrations is quite small.

The author desires to take this opportunity to thank Professor Ames and Professor Wood for the encouragement and assistance at all times most generously given. He also wishes to thank Mr. L. E. Jewell and those students who have from time to time assisted in the work, Messrs. H. S. Uhler and C. E. Melville.

Wave lengths of the principal lines and bands in the fluorescent spectrum.

Group A.

4600-5200.

Wave length	Character.	Wave length	Character.
4616.42	f	4748.55	7 b.h.
4652.04	f	4751.96	8.5
4652.18	b.h.	4753.83	8.5
4659.60	" "	4758.68	9
4684.69	fine	60.85	7 fine
4692.89	7	61.86	7 "
4704.36	1	63.05	8 "
4707.09	7	64.98	9 b.
4709.72	1	66.88	9 fine.Hs
4718.29	7	66.99	6 "
4721.33	8	70.45	7 b.
4724.42	8	71.47	7
4728.82	8	77.63	8 fine Hs
4732.77	6	81.43	10
4735.78	6 b	82.32	8 b
4736.67	8	83.35	H 10 b.
4740.95	8 fine	89.83	9 fine
4747.56	8 "	90.84	9 "

Group A.

Wave length	Character	Wave length	Character.
4793.00	10 fine Hs	4823.15	7 fine
95.30	10 b	23.82	8
99.30	10 fine	24.46	8 fine
4800.74	8 fine	25.81	7 "
02.86	8 "	26.58	8 "
04.62	10	27.27	7 "
05.77	9	27.99	8 "
06.46	6 fine	28.66	9 "
07.20	9 b	30.28	8 b.h.
07.90	7 b	32.83	8
09.93	H 8 b.h.	33.47	9 b.
10.68	10	35.36	fine
4813.68	7 fine	36.10	"
15.84	8 b	36.51	7
16.49	6 fine	36.93	7
17.14	7 fine	37.71	H broad head .5 wide
17.64	8 "	4838.92	9 b.h.
18.57	8 b.	39.88	8 b.h.
19.64	8	40.86	9
20.72	7	41.60	9
21.88	8	42.40	8 b.

Group A.

Wave length	Character	Wave length	Character.
4843.14	9 fine	4859.67	7
44.01	9 "	60.41	8
44.92	9	60.99	fine
45.83	8 fine	61.52	"
46.84	10	61.78	"
47.98	7 fine	62.21	9
49.12	7	63.02	fine
49.75	fine	63.78	6 b.h.
50.39	9	64.45	fine
51.00	fine	64.88	7 "
51.61	9	65.67	H broad .4 A.V.
52.27	fine	66.64	7
52.89	9	67.44	7
53.65	fine	68.53	7
54.35	9	69.54	8
55.06	fine	70.01	10 b.h. Hs
55.74	9	70.44	7 fine
56.54	7 fine	71.33	8 b
57.32	7 b.h.	72.05	fine
58.05	7 fine	72.59	"
58.75	8	73.01	"

Group A.

Wave length	Character	Wave length	Character.
4873.50	fine	4888.18	9
73.93	"	89.06	7
74.46	"	89.84	8
74.93	8	90.75	7
75.55	fine	91.52	9
75.95	"	92.43	7 fine
76.55	7	93.28	10 b.
77.11	8	94.13	6 fine
77.77	7 fine	95.00	H .7 A V wide
78.31	8	96.06	4
78.93	8 fine	97.02	8
79.52	9	97.92	6
80.16	8.5	98.96	7 b.h.
80.80	9.5	99.99	6
81.51	7 fine	4900.94 01.86	9 8
82.22	10		
82.93	7 fine	02.64	4 fine
83.63	10	04.96	6
84.36	7 fine	05.79	7 fine
85.17	8	06.43	4
85.88	8	07.16	7 b.h.
86.59	8	08.22	9
87.42	7 fine	08.84	fine

Group A.

Wave length	Character.	Wave length	Character.
4909.47	9	4932.20	7 fine
10.12	fine	33.03	H .7A.U.wide
10.73	8	33.70	fine
11.41	6	34.27	7
12.88	7	35.22	9
13.57	7	36.04	7
14.26	8	37.00	fine
15.09	fine	37.61	7 b.h.
15.90	9	38.80	6
16.62	6 fine	39.54	7
17.52	7 "	40.26	fine
18.27	7	40.74	"
19.10	4	41.29	"
19.99	8 fine	42.23	6 "
21.66	6 b.h.	43.16	7
22.52	6	43.82	fine
23.40	2	44.37	8
24.33	7	44.97	7
25.28	7	45.53	fine
27.11	faint	46.10	7
28.14	7	46.72	7
29.13	7	47.49	7 fine
31.22	7 fine	48.07	7 "

Group A.

Wave length	Character	Wave length	Character.
4949.24	8	4971.68	8 fine
50.08	8	72.09	"
50.83	fine	72.61	8 "
51.50	8	73.16	"
52.23	2 fine	73.70	7 "
52.97	2 "	74.28	"
54.39	10 b.	74.40	8
56.86	2	75.41	fine
57.70	2 fine	75.98	8
59.43	8	76.61	7
60.15	fine	77.17	9
61.06	6	77.85	fine
62.13	fine	78.45	8
63.02	H	79.20	4
63.80	f.h.	79.91	6
64.88	10 B.h.	80.56	7
66.81	fine	81.26	8
67.37	"	82.00	6
68.79	8 b.h.	82.65	8
69.31	fine	84.08	8
69.77	7 "	86.52	6
70.23	fine	87.18	6 fine
70.74	8 "	88.19	6
71.21	"	88.98	10 b.

Group A.

Wave length	Character	Wave length	Character.
4990.90	5	5010.24	7 fine
91.52	fine	10.68	7 "
92.56	9 b	11.26	7 "
93.34	fine	11.77	7 "
94.18	5 b.h.	12.36	7 "
95.15	4 fine	12.83	7 "
96.11	fine	13.38	7 "
96.53	"	13.99	7 "
97.29	3 b	14.50	7 "
98.05	8 b	15.13	7 "
99.25	8	15.77	7 "
5000.09	6 b	16.47	7 "
00.86	6	17.06	7 "
01.84	H .7 A U wide	17.77	7 "
02.17	fine	18.38	7 "
02.55	7 "	19.05	7 "
06.31	fine	19.68	6 "
06.90	7 "	20.42	8
07.62	7 "	21.14	6 fine
08.38	"	21.89	8
08.78	7 "	22.61	6
09.26	fine	23.37	7
09.76	7 "	24.18	6 fine

Group A.

Wave length	Character	Wave length	Character.
5024.99	7	5048.81	6
25.77	5	53.39	6 Hs
26.33	7	53.49	10 Hs
27.37	fine	54.46	8 b.h.
28.21	8	56.96	8 b.h.
28.98	7 fine	58.34	7
29.99	8	58.97	7
30.73	7 fine	61.07	7
31.76	8	62.79	7
32.53	6	63.38	8
33.47	5	64.11	fine
34.36	fine	64.84	h
35.38	7 b	66.69	7
36.33	5 b	67.37	7
37.34	8 fine	68.29	b
38.17	fine	69.08	6 b
39.52	"	69.82	7 b
40.02	"	80.38	H 10 fine
40.94	H.b.9 A U wide	87.37	H 7 b
42.58	7	95.89	9 H
43.44	fine	5118.78	Hs b.
44.93	"	26.84	b
44.59	"	33.80	Hs b
		41.27	Hs b.

Group C. 5300-5700.

The lines of this group are all of about the same intensity and very faint. Only the strong lines of intensity 8 or greater are marked.

Wave length	Character.	Wave length	Character.
5269.38		5384.33	
75.34		90.46	
79.58		91.41	
5305.68		97.77	
11.47		98.46	
17.65		5402.61	
25.64		03.90	
30.61		09.78	
34.85		14.96	
37.70		16.52	
43.66		18.90	
46.47		25.42	
49.67		26.20	
52.44		32.68	
58.36		33.63	
65.31		39.25	
66.09		40.33	
70.28		41.36	
71.23		48.20	
78.19		52.94	
82.12		58.09	
83.38		63.11	

Group C.

Wave length	Character.	Wave length	Character.
5482.21		5602.04	broad
96.99		03.34	"
5502.48		07.60	
23.48		12.31	
28.58		13.78	
30.44		19.09	strong 8
33.16		20.56	"
35.89		26.31	"
40.03		28.13	"
59.52		32.79	
62.85		36.90	
64.28		38.02	
65.70		41.18	
72.53		42.26	
74.82		43.55	broad
75.90		45.37	"
76.81		46.92	"
81.86		48.78	
83.07		49.60	
84.59		51.94	borad & strong 8
93.45	strong 8	52.80	strong
94.87	" 8	54.27	"

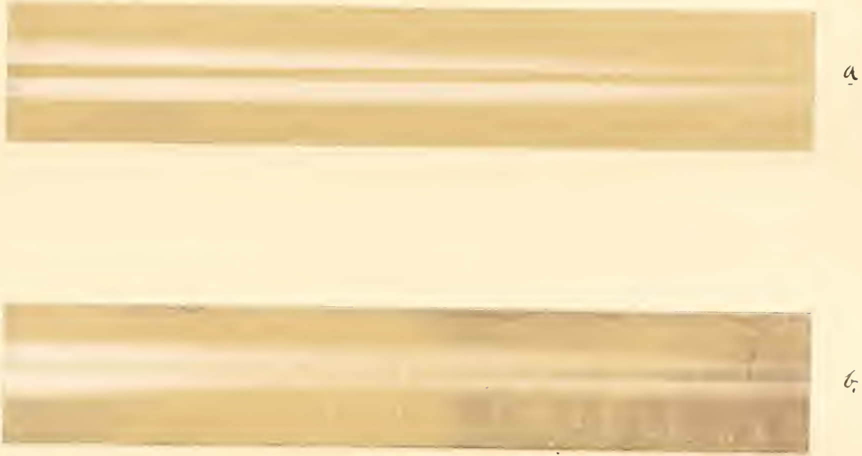
Group C.

Wave length	Character.
5655.83	
59.97	strong
64.12	
65.63	broad
71.25	
72.68	strong 8
79.03	" 8
83.01	" 8
84.30	
89.70	
97.87	strong & broad 9
5706.08	" " 9
10.84	" 8
12.48	
13.56	
14.72	
17.23	
18.05	
20.82	
34.78	
36.89	
38.32	

Wave lengths of principal lines and bands in the Fluorescent Spectrum.

Wave length	Character	Wave length	Character.
4660		5041	H
4671		5053	Hs
4685		5081	H band
4693		5087	H
4707		5096	H
18		5109	
32		5119	Hs
41		5127	
54		5134	Hs band
69		5142	Hs
83	H	5154	
93	Hs	5174	band hazy.
4810	H	82	
4820		90	
4838	H	5203	
4849		5228	
4866	H	40	band. hazy
4895	H	53	
4914		5280	
4933	H	95	band. hazy
4963	H	5311	
4981		5349	center of hazy band.
5002	H		

Plate I

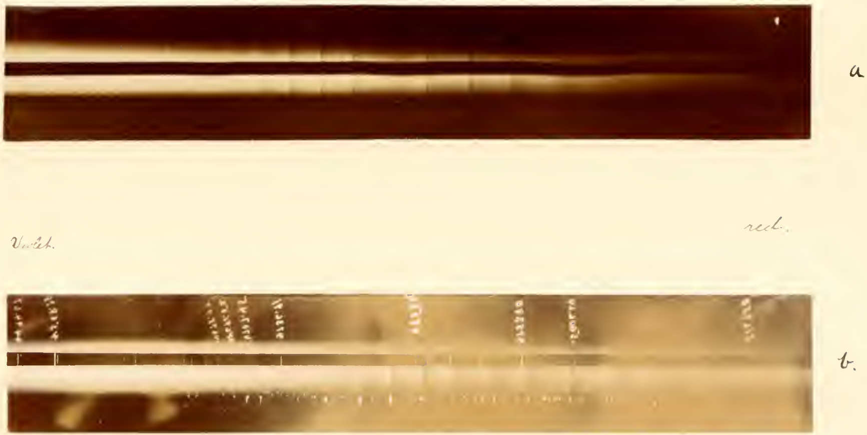


a- Channels. 5200 - 4600. as they first appear.

b- same region, with denser vapour.

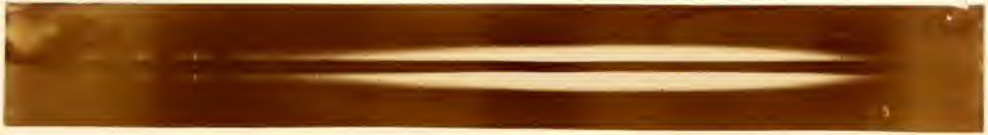
* longer wave lengths to the right.

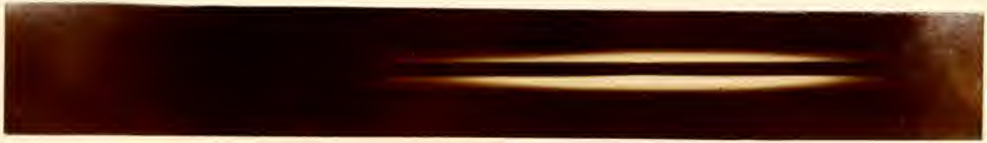
Plate. II.



a and b Channels (5200 - 4600) when vapour is denser
than in Plate I.

Plate III

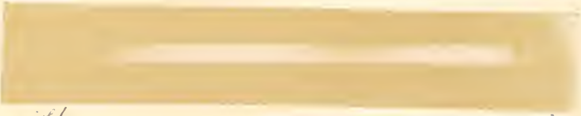




a- 5300-5700 when vapour density is slightly increased from condition in Plate II. The channels are visible on the left.

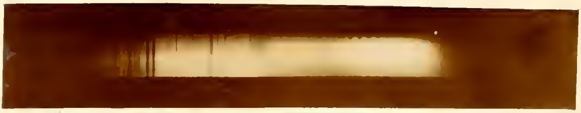
b- A further increase in vapour density. band narrows up.

Plate IV



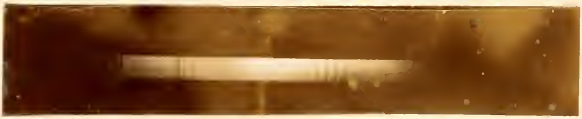
a

a- absorption spectrum with small grating.
vapour dense enough to bring out channels 5300-4600
D line absorption band on the right.



b.

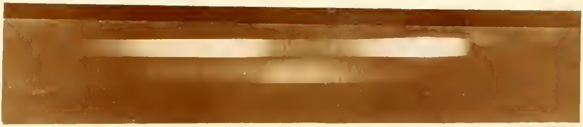
b- Fluorescent spectrum with small grating
showing channels 5300-4600. and the solar lines K
and H on left.



c.

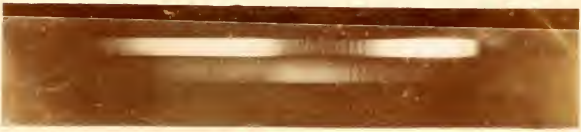
c- Fluorescent spectrum. in which the channels
can be traced farther toward the violet.

Plate V



a

a. - Upper spectrum absorption
lower " fluorescent



b.

b. same as a, but showing the blue channels in the fluorescent spectrum.

BIOGRAPHY.

Joseph Haines Moore, son of John Haines and Mary Haines Moore, was born in Wilmington, Clinton Co.,Ohio, on September 7, 1878. He received his preliminary instruction in a public school of his native city, and in the preparatory department of Wilmington College. Later he followed the classical course in Wilmington College, receiving from that institution the B. A. degree in 1897. The following year was spent in graduate work in the same College in Astronomy. In 1898 he entered Johns Hopkins University, where he has since followed graduate courses in Physics, Mathematics and Astronomy. During the year 1901-1902 he held a University Scholarship.